

Hybrid catalysts with enhanced C<sub>3</sub>H<sub>6</sub> resistance for NH<sub>3</sub>-SCR of NO<sub>x</sub>Qi Zhao<sup>a</sup>, Bingbing Chen<sup>a</sup>, Zhifeng Bai<sup>a</sup>, Limei Yu<sup>a</sup>, Mark Crocker<sup>b,\*</sup>, Chuan Shi<sup>a,\*</sup><sup>a</sup> State Key Laboratory of Fine Chemicals, School of Chemistry, Dalian University of Technology, Dalian, 116024, China<sup>b</sup> Center for Applied Energy Research, University of Kentucky, Lexington, KY, 40511, USA

## ARTICLE INFO

## Keywords:

NH<sub>3</sub>-SCR

Propene poisoning resistance

Fe-Beta

MnO<sub>x</sub>/CeO<sub>2</sub>

DRIFTS

## ABSTRACT

Utilization of Fe-Beta for NH<sub>3</sub>-SCR of NO<sub>x</sub> in diesel engine applications is severely limited by hydrocarbon poisoning. In this work, a series of hybrid catalysts are prepared by mechanical mixing of zeolites and oxides, and their activity for the selective catalytic reduction of NO<sub>x</sub> with NH<sub>3</sub> is investigated in the presence of propene. Results have shown that a catalyst prepared by mixing Fe-Beta and MnO<sub>x</sub>/CeO<sub>2</sub> in a mass ratio of 1:1 exhibits high SCR activity. NO<sub>x</sub> conversion in the temperature range 200–400 °C has exceeded 90% at a GHSV of 80,000 h<sup>-1</sup>, with low selectivity to N<sub>2</sub>O. By the combined DRIFTS and MS measurements, the function of MnO<sub>x</sub>/CeO<sub>2</sub> in the hybrid catalysts is discussed. This hybrid catalyst is able to convert C<sub>3</sub>H<sub>6</sub> to intermediates containing C=O and COO functionalities, thereby decreasing carbon deposition on the zeolite and reduce the competitive adsorption between C<sub>3</sub>H<sub>6</sub> and NO<sub>x</sub>. Moreover, these intermediates react with NO<sub>x</sub> at lower temperatures than do the carbonaceous deposits on Fe-Beta, enhancing the NO<sub>x</sub> reduction activity.

## 1. Introduction

Selective catalytic reduction (SCR) by urea or ammonia is one of the most commonly applied technologies for the abatement of nitrogen oxides (NO<sub>x</sub>) in the presence of excess oxygen [1]. Metal exchanged zeolites, which in recent years have attracted much attention in the field of NH<sub>3</sub>-SCR, are commercial catalysts used for automobile exhaust purification, normally exhibiting excellent performance over a wide temperature range (200–650 °C) [1–4].

Fe-containing zeolites, especially for Fe-Beta catalysts, present better high temperature activities compared with commercial Cu-SSZ-13 catalysts, with the former typically displaying better resistance to sulfur poisoning [1,5,6]. By employing Al-rich Beta zeolites as a substrate for Fe, low temperature activity (≤200 °C) can be maximized, enabling the application of Fe-Beta catalysts in NH<sub>3</sub>-SCR of NO<sub>x</sub> [1,7,8]. However, owing to the fact that Beta zeolites possess relatively large pores and cages than SSZ-13 (pore diameters of approximately 6.5 Å and 3.8 Å, respectively), catalyst activity is inhibited in the presence of hydrocarbons which possess small kinetic diameters (such as propene, 4.5 Å) due to coke deposition in the zeolite channels [3,9]. Besides the effect of intrinsic pore structure, zeolites with strong acidity are more susceptible towards deactivation by hydrocarbons, because hydrocarbons can adsorb on the acid sites to ultimately form coke deposits [10,11]. In recent years, the poisoning of SCR catalysts by hydrocarbons and possible methods to reduce the consequences have been

studied by a number of researchers [10,12–17]. Luo et al. [18] found that dodecane decreased Cu-Beta's NH<sub>3</sub>-SCR activity at 150 °C due to its physical adsorption in the zeolite pores that blocked access to active sites. Ma et al. [10] designed a novel fully formulated Fe-BEA monolith catalyst coating modified with MOR, the deactivation of Fe-BEA due to propene poisoning being clearly reduced.

On the other hand, manganese - based oxide catalysts not only exhibit particularly high activity for low temperature NH<sub>3</sub>-SCR, but also act as superior oxidation catalysts for a variety of volatile organic compounds (VOCs) combustion reactions [19–21]. Inspired by the dual properties of manganese - based catalysts, we propose a novel approach to reduce the negative effects of C<sub>3</sub>H<sub>6</sub> on Fe-Beta catalysts by mechanical mixing of MnO<sub>x</sub>/CeO<sub>2</sub> oxide with Fe-Beta zeolite. The reason for choosing CeO<sub>2</sub> as co-component is that ceria is potentially advantageous for NH<sub>3</sub>-SCR, e.g. broadening the SCR temperature window, enhancing high temperature activity and improving N<sub>2</sub> selectivity and resistance to poisoning by SO<sub>2</sub> [19,22–24]. Hypothetically, the oxide can oxidize C<sub>3</sub>H<sub>6</sub> and consequently reduce its inhibiting effect on the NH<sub>3</sub>-SCR reaction. As we shown in this paper, hybrid catalysts consisting of MnO<sub>x</sub>/CeO<sub>2</sub> mixed with Fe-Beta (with optimized mass ratios) do indeed greatly improve SCR activity in the presence of C<sub>3</sub>H<sub>6</sub>, albeit the mechanism behind the enhancement is not exactly as anticipated. Based on in situ DRIFTS measurements, combined with MS studies, the roles of MnO<sub>x</sub>/CeO<sub>2</sub> and Fe-Beta zeolite in NH<sub>3</sub>-SCR in the presence of C<sub>3</sub>H<sub>6</sub> were clarified in the present study.

\* Corresponding authors.

E-mail addresses: [mark.crocker@uky.edu](mailto:mark.crocker@uky.edu) (M. Crocker), [chuanshi@dlut.edu.cn](mailto:chuanshi@dlut.edu.cn) (C. Shi).<https://doi.org/10.1016/j.apcatb.2018.09.072>

Received 11 June 2018; Received in revised form 15 September 2018; Accepted 21 September 2018

Available online 26 September 2018

0926-3373/ © 2018 Elsevier B.V. All rights reserved.

## 2. Experimental

### 2.1. Catalyst preparation

The zeolite support was organotemplate-free Na-Beta zeolite with a Si/Al ratio of 9 which was obtained from BASF, Germany. The synthesis of this zeolite has been reported elsewhere [25]. Before use, Na-Beta underwent a conventional ion-exchange process to bring it into the  $\text{NH}_4^+$  form. Using  $\text{NH}_4$ -Beta as precursor, a 2 wt% iron-containing zeolite catalyst was prepared by incipient wetness impregnation (IWI) with a solution of ferrocene in toluene at room temperature, followed by calcination at 500 °C in air for 4 h using a heating rate of 4 °C min<sup>-1</sup>. This material is henceforth referred to as Fe-Beta.

The  $\text{MnO}_x/\text{CeO}_2$  catalyst was prepared by a deposition – precipitation method. Typically, an appropriate amount of aqueous Mn ( $\text{NO}_3$ )<sub>2</sub> solution was mixed with  $\text{CeO}_2$  powder (Rare - Chem Hi - Tech Co., Ltd., China), and then an aqueous solution of  $\text{Na}_2\text{CO}_3$  was added dropwise under continuous stirring until the pH reached 8.5–9.0. The precipitate was aged for 1 h at room temperature, after which the mixture was filtered and washed with deionized water. The resulting solid was dried at 110 °C and then calcined in air at 400 °C for 4 h. The target Mn concentration was determined to be 50 wt%. Pure manganese oxide was prepared by the same procedure used for  $\text{MnO}_x/\text{CeO}_2$ , except for the addition of the  $\text{CeO}_2$  support.

The hybrid catalysts were prepared by mechanically grinding different amounts of Fe-Beta and oxides, followed by calcining the mixtures at 500 °C in air. The hybrid catalysts were denoted as follows: FM = Fe-Beta +  $\text{MnO}_x$  (with a mass ratio of 3:1); FC = Fe-Beta +  $\text{CeO}_2$  (with a mass ratio of 3:1); FMC1 to FMC3 = Fe-Beta +  $\text{MnO}_x/\text{CeO}_2$  for which the mass ratio of zeolite and oxide was varied from 1:1 to 3:1. All samples were pressed, crushed, and sieved to 40–60 mesh to obtain suitable particles for the experiments.

### 2.2. Catalyst characterization

X-ray diffraction (XRD) measurements were carried out on an X-ray diffractometer (Rigaku D/Max 2400) with Cu K $\alpha$  radiation ( $\lambda = 1.5404 \text{ \AA}$ ) in a  $2\theta$  range of 5–90° at a scanning speed of 0.02° s<sup>-1</sup>.

Hydrogen temperature programmed reduction ( $\text{H}_2$ -TPR) experiments were performed on a Micromeritics AutoChem II 2920 chemisorption analyzer. A sample of ~50 mg was placed in a U-shape quartz reactor. The catalysts were first pretreated at 300 °C in Ar for 1 h, then cooled down to the room temperature. Subsequently, a mixture of 5%  $\text{H}_2/\text{Ar}$  (100 ml min<sup>-1</sup>) was fed to the reactor and the temperature was linearly increased to 600 °C at a rate of 10 °C min<sup>-1</sup>.

X-ray photoelectron spectroscopic (XPS) measurements were conducted by ESCALAB250 Thermo VG spectroscopy using an Al K $\alpha$  source operating at 15 kV and 10 mA. C 1s at 284.6 eV was used as an internal binding energy standard to correct for charging effects.

### 2.3. Techniques

In situ DRIFTS measurements were performed on a Bruker Tensor 27 spectrometer equipped with MCT detector. The catalyst was first pretreated in He at 300 °C for 1 h, then cooled down to the test temperature, and a background spectrum was recorded at each measured temperature under flowing of He.  $\text{NH}_3$ ,  $\text{C}_3\text{H}_6$  +  $\text{O}_2$ ,  $\text{NO}$  +  $\text{C}_3\text{H}_6$  +  $\text{O}_2$  and  $\text{NO}$  +  $\text{O}_2$  adsorption were performed by flowing the appropriate gas for 0.5 h and then purging with He for another 15 min at the same temperature. After the adsorption and purging steps, the He flow was switched to other flowing gases to achieve a so-called transient surface reaction, e.g.,  $\text{NH}_3 \rightarrow \text{NO} + \text{O}_2$ , or  $\text{NH}_3 \rightarrow \text{NO} + \text{O}_2 + \text{C}_3\text{H}_6$ . DRIFT spectra were then recorded periodically as a function of reaction time, 60 scans being accumulated in each case at a resolution of 4 cm<sup>-1</sup>.

Identical transient procedures were carried out using an online mass spectrometer (MS, Omini-star, GSD-300) to detect the effluent gases

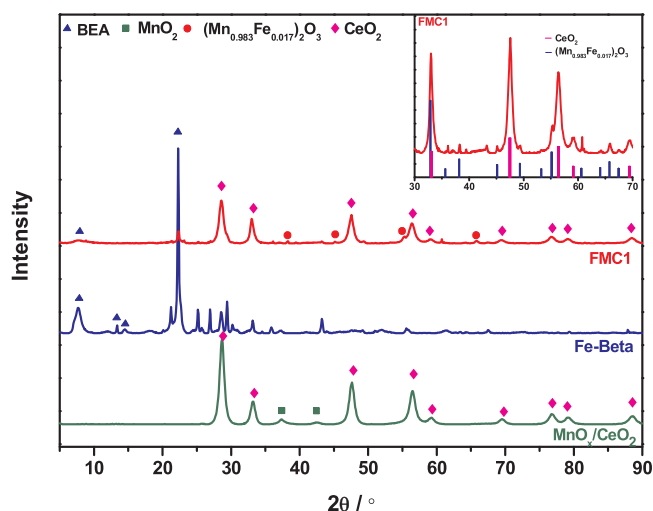


Fig. 1. XRD patterns of the indicated catalysts.

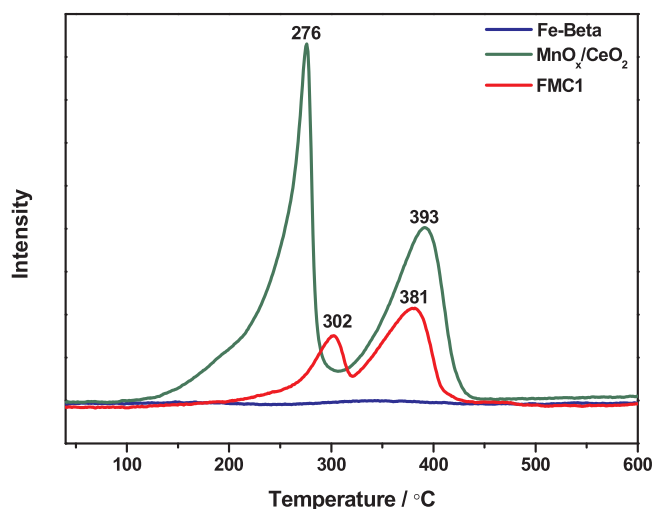


Fig. 2.  $\text{H}_2$ -TPR profiles of different catalysts. Conditions: 5%  $\text{H}_2/\text{Ar}$ ; flow rate: 100 ml/min; ramp rate: 10 °C/min.

during the surface reaction. The masses characteristic of NO (30),  $\text{NH}_3$  (17),  $\text{O}_2$  (32),  $\text{N}_2$  (28, 14),  $\text{H}_2\text{O}$  (18),  $\text{N}_2\text{O}$  (29, 44, 45), CO (14, 28),  $\text{CO}_2$  (22, 44, 45),  $\text{C}_3\text{H}_6$  (41, 42),  $\text{NO}_2$  (46) were recorded. Competitive adsorption experiments were conducted by using 50 mg catalyst in a quartz reactor. The adsorption was performed by passing a gas mixture containing 500 ppm NO and 5%  $\text{O}_2$ , or 500 ppm NO, 500 ppm  $\text{C}_3\text{H}_6$ , 5%  $\text{O}_2$  and Ar as balance gas through the sample bed at RT for 1 h with the total flow rate of 200 ml min<sup>-1</sup>. After the adsorption, the system was purged with Ar until no  $\text{NO}_x$  or  $\text{C}_3\text{H}_6$  were detected in the effluent. TPD measurements were carried out up to 700 °C with a heating rate of 10 °C min<sup>-1</sup> in flowing of Ar.

### 2.4. Catalytic activity measurements

The  $\text{NH}_3$ -SCR activity measurements were conducted with 180 mg of the sample using a fixed-bed quartz microreactor (i.d. 6 mm). Before each experiment, the catalyst was first pretreated in  $\text{N}_2$  for 1 h at 500 °C, and then cooled down to desired temperature. Then the catalyst was exposed to a reactant gas mixture containing 500 ppm NO, 500 ppm  $\text{NH}_3$ , 500 ppm  $\text{C}_3\text{H}_6$  (when used), 10%  $\text{O}_2$ , 10%  $\text{CO}_2$ , 5%  $\text{H}_2\text{O}$  and balanced  $\text{N}_2$ , and the total flow rate was 400 ml min<sup>-1</sup>. NO,  $\text{NO}_2$ ,  $\text{NO}_x$  (= NO +  $\text{NO}_2$ ),  $\text{NH}_3$  and  $\text{N}_2\text{O}$  concentrations were monitored continuously using a  $\text{NO}_x$  analyzer (Ecophysics, Switzerland) and an  $\text{NH}_3$ /

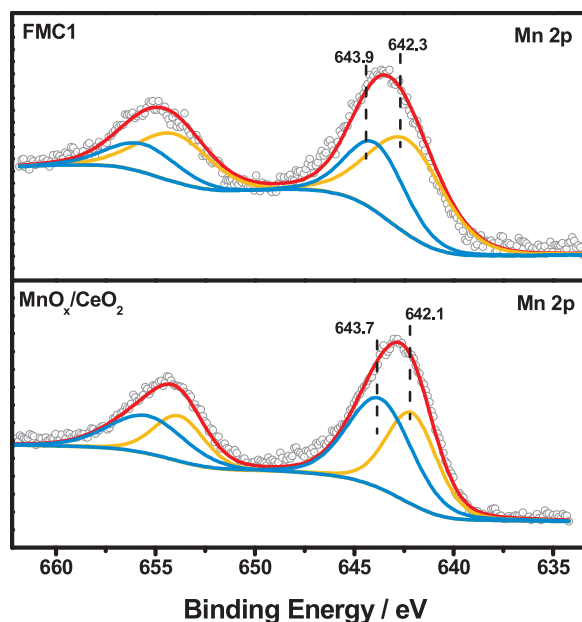


Fig. 3. XPS spectra of  $\text{MnO}_x/\text{CeO}_2$  and FMC1 in the Mn 2p region.

$\text{N}_2\text{O}$  analyzer (Sick Maihak, Germany), respectively. All data were obtained when the SCR reaction reached a steady state at each temperature.  $\text{C}_3\text{H}_6$  oxidation activity was monitored by an online non-dispersive infrared analyzer (SICK-MAIHAK-S710, Germany) which recorded the concentration of CO and  $\text{CO}_2$ . A Cu-Mn/ $\text{Al}_2\text{O}_3$  catalyst was used to completely oxidize  $\text{C}_3\text{H}_6$  into  $\text{CO}_x$  at 500 °C [26,27], the amount of  $\text{CO}_x$  generated being used to quantify the  $\text{C}_3\text{H}_6$  concentration.

### 3. Results and discussion

#### 3.1. Catalyst structural characterization

In order to ascertain whether any structural transformations occurred during mechanical mixing of the catalyst components, sample FMC1 was subjected to analysis. For reference purposes, Fe-Beta and  $\text{MnO}_x/\text{CeO}_2$  were also analyzed.

XRD patterns for the samples are displayed in Fig. 1. The characteristic reflections of the BEA framework [25] and  $\text{CeO}_2$  (JCPDS no. 43-1002) can both be observed for the FMC1 sample. Notably, the X-ray

peak intensity of  $\text{CeO}_2$  is relatively higher than that of  $\text{MnO}_x$ . As indicated in the slow scan XRD pattern from 26 to 31° (Fig. S1), a shift of the diffraction peak to higher Bragg angles can be observed for  $\text{MnO}_x/\text{CeO}_2$  with respect to  $\text{CeO}_2$  [28]. The lattice constant calculated for  $\text{CeO}_2$  is 5.410 Å, while that for  $\text{MnO}_x/\text{CeO}_2$  is 5.404 Å. Hence, the observed decrease in the lattice constant is evidence of the formation of a Mn-Ce-O solid solution [29,30]. However, due to the high fraction of  $\text{MnO}_x$  in  $\text{MnO}_x/\text{CeO}_2$ , a discrete manganese oxide phase is present on the catalyst surface, giving rise to  $\text{MnO}_x$  diffraction peaks. After mechanical mixing of Fe-Beta with  $\text{MnO}_x/\text{CeO}_2$ , the reflections for Fe-Beta have become extremely weak, the  $\text{CeO}_2$  reflections being much stronger compared to Fe-Beta. This might be related to coating of the zeolite by  $\text{MnO}_x/\text{CeO}_2$  particles, as shown by TEM images (Fig. S2), leading to the lower intensity of zeolite diffraction lines. Similar results have been reported in the literature [17]. In addition, a new phase corresponding to  $(\text{Mn}_{0.983}\text{Fe}_{0.017})_2\text{O}_3$  (JCPDS no. 24-0507) is detected, as clearly shown in the inset figure. This suggests that chemical interactions occur between Fe-Beta and  $\text{MnO}_x/\text{CeO}_2$  upon calcination.

Fig. 2 shows  $\text{H}_2$ -TPR profiles recorded for FMC1, Fe-Beta and  $\text{MnO}_x/\text{CeO}_2$ . There are two major  $\text{H}_2$  consumption peaks at 302 °C and 381 °C for the FMC1 sample. By comparison with the profile of  $\text{MnO}_x/\text{CeO}_2$ , the peak at 381 °C can be assigned to the reduction of  $\text{Mn}^{3+}$  to  $\text{Mn}^{2+}$  [21,31]. Relative to  $\text{MnO}_x/\text{CeO}_2$ , the first peak is weaker and shifted to higher temperature, and can be ascribed to the formation of the  $(\text{Mn}_{0.983}\text{Fe}_{0.017})_2\text{O}_3$  phase which leads to a change in the chemical states of Mn. This has been further confirmed by XPS results shown in Fig. 3.

Two kinds of Mn species are present in XPS profiles (Fig. 3). The peak at BE = 642.1–642.3 eV can be assigned to  $\text{Mn}^{3+}$  [32,33], while that at BE = 643.7–643.9 eV is assigned to  $\text{Mn}^{4+}$  [33,34]. Deconvolution of the peaks enables the distribution of Mn species to be estimated. The ratio of  $\text{Mn}^{3+}/(\text{Mn}^{3+} + \text{Mn}^{4+})$  is 63.5% for FMC1, which is higher than that of  $\text{MnO}_x/\text{CeO}_2$  (44.6%), indicating that FMC1 is enriched with  $\text{Mn}^{3+}$ .

#### 3.2. Catalytic activity

$\text{NO}_x$  conversion and  $\text{N}_2\text{O}$  yield as a function of reaction temperature over the Fe-based catalysts are shown in Fig. 4.  $\text{NH}_3$ -SCR activity below 300 °C is severely depressed by the presence of  $\text{C}_3\text{H}_6$  in the feed gas over Fe-Beta catalyst (Fig. 4(A)), as compared to the experiment with no hydrocarbon present (shown as a grey dotted line in Fig. 4(A)). The activity of the hybrid catalysts, corresponding to  $\text{CeO}_2$ ,  $\text{MnO}_x$ , and  $\text{MnO}_x/\text{CeO}_2$  mixed with Fe-Beta zeolite at a fixed weight ratio of 1:3, is

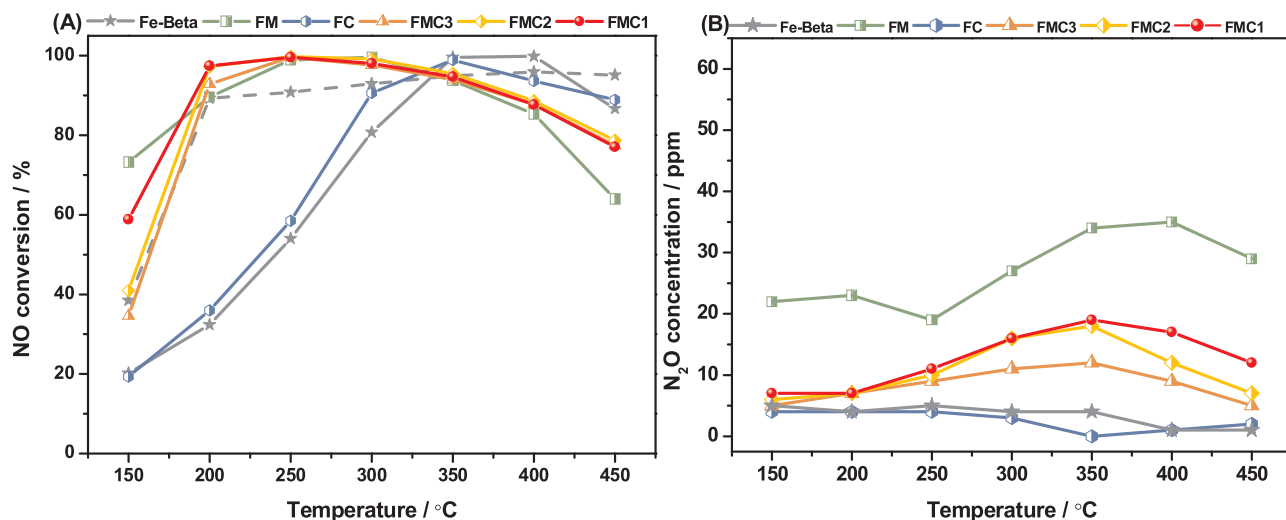


Fig. 4.  $\text{NH}_3$ -SCR performance in the presence of  $\text{C}_3\text{H}_6$  (A) and  $\text{N}_2\text{O}$  yield (B) of the indicated catalysts, the activity of Fe-Beta in the absence of  $\text{C}_3\text{H}_6$  being shown as the grey dotted line in the figure. Conditions: 500 ppm NO, 500 ppm  $\text{NH}_3$ , 500 ppm  $\text{C}_3\text{H}_6$ , 10%  $\text{O}_2$ , 10%  $\text{CO}_2$ , 5%  $\text{H}_2\text{O}$  and  $\text{N}_2$  balance, GHSV = 80,000  $\text{h}^{-1}$ .

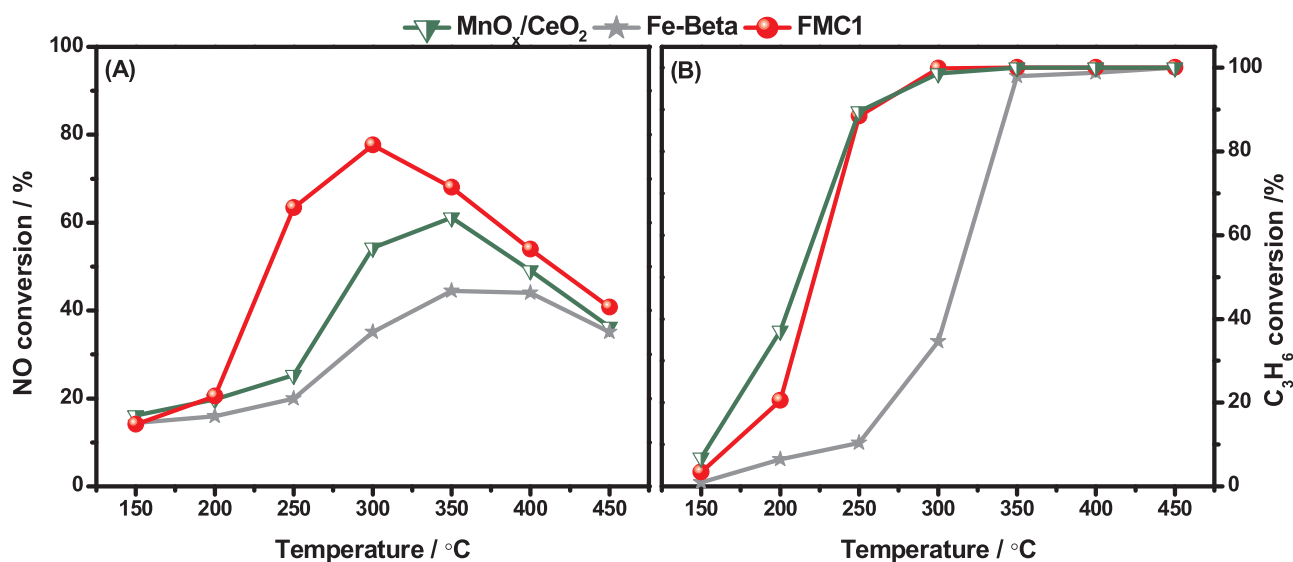


Fig. 5.  $C_3H_6$ -SCR (A) and  $C_3H_6$  oxidation activity (B) of the indicated catalysts. Conditions: (A) 500 ppm NO, 500 ppm  $C_3H_6$ , 10%  $O_2$ , 10%  $CO_2$ , 5%  $H_2O$  and  $N_2$  balance, (B) 500 ppm  $C_3H_6$ , 10%  $O_2$  and  $N_2$  balance, GHSV =  $80,000\ h^{-1}$ .

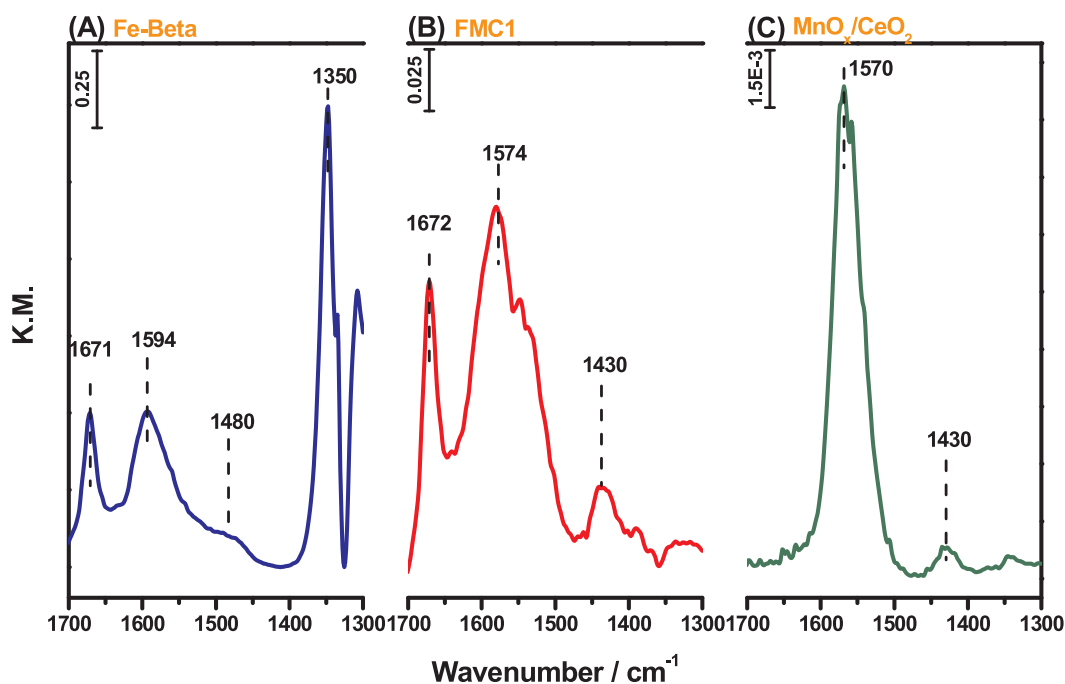


Fig. 6. IR spectra of (A) Fe-Beta, (B) FMC1 and (C)  $MnO_x/CeO_2$  after exposure to 500 ppm  $C_3H_6$ /10%  $O_2$ /He at  $150^\circ C$  for 30 min.

also evaluated. Although addition of  $CeO_2$  to Fe-Beta zeolite has little influence on the activity, mixing Fe-Beta with  $MnO_x$  improved the low temperature activity.  $NO_x$  conversion over FM and FMC3 has reached 73.3% and 34.6% at  $150^\circ C$  respectively. Upon further increase of the temperature,  $NO_x$  conversion has decreased gradually, especially over the FM catalyst, which should be due to the occurrence of a side reaction of  $NH_3$  oxidation catalyzed by  $MnO_x$ . Meanwhile, significant  $N_2O$  formation is observed over FM compared with FC and FMC3. The yield of  $N_2O$  (shown in Fig. 4(B)) has presented two basic trends in the present study:  $N_2O$  has been observed to increase with temperature as well as with the fraction of  $MnO_x$  in the catalyst, indicating that  $N_2O$  has been formed from the  $NH_3$  oxidation reaction, which is preferentially catalyzed by  $MnO_x$  and favored at higher temperature [35]. In addition, it is known that  $MnO_x/CeO_2$  possesses better  $SO_2$  resistance than  $MnO_x$  itself and thus FMC3 exhibited better  $SO_2$  resistance than

FM, as shown in Fig. S3 [36]. Given these trends,  $MnO_x/CeO_2$ , as opposed to  $MnO_x$ , has been employed for this study, the ratio of Fe-Beta to  $MnO_x/CeO_2$  being optimized. Upon decrease of the weight ratio of the zeolite to mixed oxide from 3:1 to 1:1, the low temperature activity has been greatly enhanced,  $NO$  conversions of 58.8% and 96.9% being obtained at  $150^\circ C$  and  $200^\circ C$  respectively. Moreover, better high temperature activity has also been obtained for FMC1 compared with other hybrid catalysts. These results give clear evidence that the mixture of  $MnO_x/CeO_2$  oxide with Fe-Beta zeolite provides simple and effective approach for maintaining the superior performance of Fe-Beta zeolite in  $NH_3$ -SCR in the presence of  $C_3H_6$ .

The catalytic performance of Fe-Beta,  $MnO_x/CeO_2$  and FMC1 in  $C_3H_6$ -SCR of  $NO_x$  and  $C_3H_6$  oxidation has also been evaluated in an attempt to ascertain whether  $MnO_x/CeO_2$  catalyzed the  $C_3H_6$ -SCR of  $NO_x$  directly or whether it was responsible for oxidation of  $C_3H_6$  to  $CO_x$ ,

**Table 1**  
Assignments of FTIR bands observed during related reaction process.

Species	Wavenumber (cm <sup>-1</sup> )	
	References	This work
$\nu_s(\text{COO})$	1430–1457 [37,38]	1430
$\nu_{as}(\text{COO})$	1540–1580 [37,38]	1570–1574
$\nu(\text{C}=\text{C})$ in $\pi\text{-C}_3\text{H}_5$	1490–1510 [39,40]	1480
$\nu(\text{C}=\text{C})$ in allylic	1372–1379 [40,41]	1350
$\nu(\text{C}=\text{C})$ in polyene	1605–1590 [39,40,42]	1594
$\nu(\text{C}=\text{O})$	1668, 1684–1725 [43,44,45]	1670–1695
$\text{NH}_4^+$	1465–1470 [46,47,48]	1474–1485
Coordinated $\text{NH}_3$	1602–1610 [33,46,47,49]	1600–1620
$\nu_s(\text{NO}_2)$	1320 [50]	1313–1334
$\nu(\text{NO}_3^-)$	1293, 1320, 1550–1684 [38,43,46,47,50,51]	1280, 1430–1447, 1530, 1570, 1583, 1602, 1629
$\nu_{as}(\text{NO}_2)$	1420–1500 [50]	1480
$\nu(\text{N}_2\text{O}_3)$	1684 [47]	1684
$\nu(\text{NO}_2)$	1675 [46]	1668
Gaseous NO	1878 [46,47]	1870–1880
$\nu(\text{CH}_3)$	2890–2924 [40,42,44]	2926

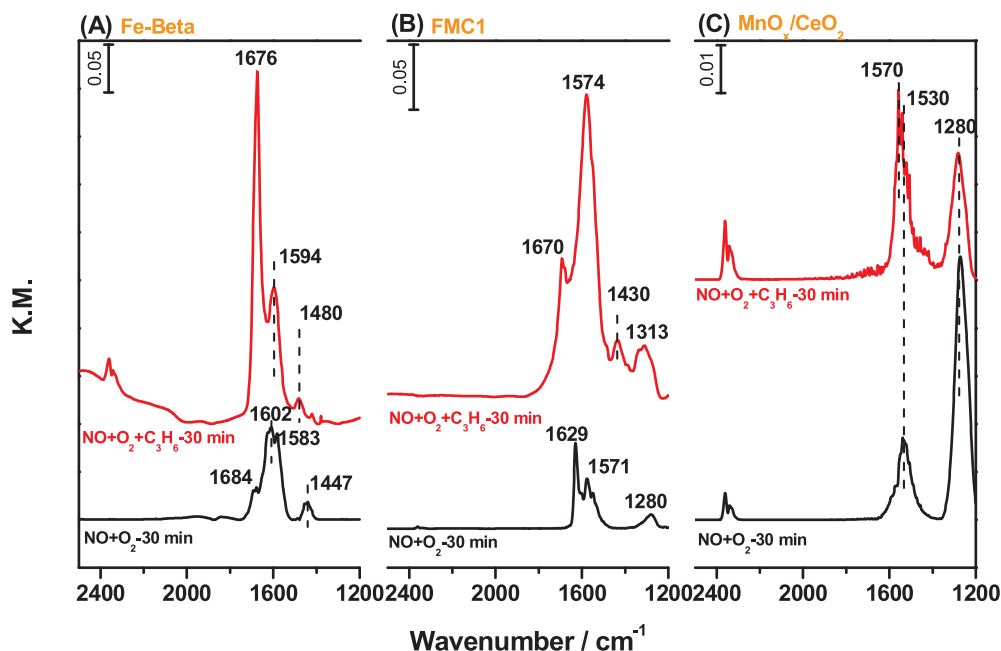
thereby eliminating the negative effects of  $\text{C}_3\text{H}_6$  on Fe-Beta. In the case of  $\text{C}_3\text{H}_6$ -SCR, as shown in Fig. 5(A),  $\text{NO}_x$  conversion over all three of the catalysts is quite poor at temperatures below 250 °C. For example,  $\text{NO}_x$  conversion is 20.5% over FMC1 at 200 °C, much lower than the 97.4%  $\text{NO}_x$  conversion observed in  $\text{NH}_3$ -SCR. This suggests that the improvement in low temperature activity induced by the mixed oxide is not a consequence of the  $\text{C}_3\text{H}_6$ -SCR reaction. For  $\text{C}_3\text{H}_6$  oxidation, as shown in Fig. 5(B), the conversions obtained below 200 °C are also quite poor for all of the catalysts. The  $\text{C}_3\text{H}_6$  conversion over FMC1 catalyst is below 20% at 200 °C, which indicates that the enhanced activity resulting from addition of the mixed oxide (especially at temperatures below 200 °C) can not be ascribed to the direct combustion of  $\text{C}_3\text{H}_6$  into  $\text{CO}_x$  ( $x = 1$  or 2). In addition, it is noteworthy that a 50% yield of CO has been obtained over Fe-Beta, in comparison to CO yields of less than 5% over the mixed oxide and hybrid catalysts due to their higher activity for oxidation as shown in Fig. S4. The fact that CO is generated as a secondary pollutant over Fe-Beta when  $\text{C}_3\text{H}_6$  is presented, highlights the benefits of applying the catalyst mixture in the  $\text{NH}_3$ -SCR reaction.

### 3.3. Co-adsorption of $\text{C}_3\text{H}_6 + \text{O}_2$

The function of the mixed oxide in the  $\text{NH}_3$ -SCR reaction has been examined by coupling in situ DRIFTS for the detection of surface intermediates and MS for the analysis of gas phase species. Fig. 6 shows IR spectra of Fe-Beta,  $\text{MnO}_x/\text{CeO}_2$  and FMC1 after exposure to 500 ppm  $\text{C}_3\text{H}_6 + 10\% \text{O}_2$  for 30 min at 150 °C followed by purging in He for another 15 min. The detailed descriptions of IR bands are displayed in Table 1. For the Fe-Beta sample, four bands appeared, which are assigned to  $\nu(\text{C}=\text{O})$  (1671  $\text{cm}^{-1}$ ),  $\nu(\text{C}=\text{C})$  in a polyene (1594  $\text{cm}^{-1}$ ),  $\nu(\text{C}=\text{C})$  in  $\pi\text{-C}_3\text{H}_5$  (1480  $\text{cm}^{-1}$ ) and  $\nu(\text{C}=\text{C})$  in an allylic group (1350  $\text{cm}^{-1}$ ). These results indicate that  $\text{C}_3\text{H}_6$  is adsorbed on the Fe-Beta surface and that adsorbed  $\text{C}_3\text{H}_6$  is apt to polymerize as evidenced by the presence of polyene,  $\pi\text{-C}_3\text{H}_5$  and allylic groups. The presence of such polymerized species can be expected to result in blocking of the zeolite pores. In the case of FMC1, the main peaks observed belong to  $\nu(\text{C}=\text{O})$  (1672  $\text{cm}^{-1}$ ),  $\nu_s(\text{COO})$  (1574  $\text{cm}^{-1}$ ) and  $\nu_{as}(\text{COO})$  (1430  $\text{cm}^{-1}$ ), suggesting that  $\text{C}_3\text{H}_6$  is partially oxidized on the catalyst to form adsorbed oxygenates. After saturation with  $\text{C}_3\text{H}_6 + \text{O}_2$  for 30 min over the  $\text{MnO}_x/\text{CeO}_2$  oxide, only two peaks can be observed which can be assigned to carboxyl species. From these results, it is clear that FMC1 and  $\text{MnO}_x/\text{CeO}_2$  are more active than Fe-Beta for  $\text{C}_3\text{H}_6$  oxidation, preventing the polymerization of  $\text{C}_3\text{H}_6$  on the Fe-Beta zeolite.

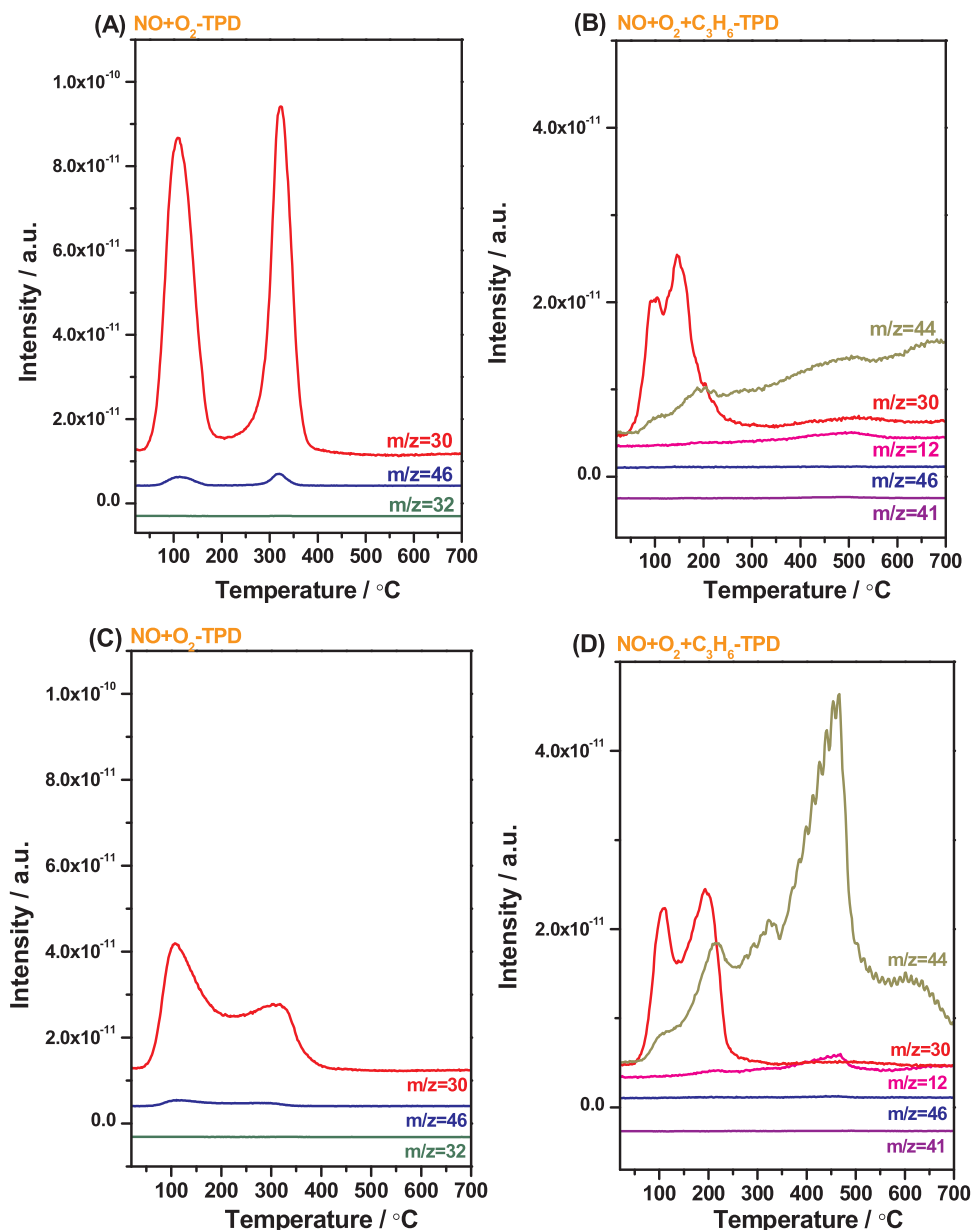
### 3.4. Competitive adsorption of $\text{NO}_x$ with $\text{C}_3\text{H}_6$

In situ DRIFTS studies of  $\text{NO} + \text{O}_2$  adsorption on Fe-Beta, FMC1 and  $\text{MnO}_x/\text{CeO}_2$  have been carried out, both with and without  $\text{C}_3\text{H}_6$ , the results being shown in Fig. 7. Upon exposure of Fe-Beta, peaks at 1684, 1602, 1583 and 1447  $\text{cm}^{-1}$  are observed. These bands are attributed to the asymmetric stretching frequency of gaseous  $\text{NO}_2$ , overlapped with bands due to bridged nitrate (1602  $\text{cm}^{-1}$ ), bidentate nitrate and monodentate nitrate (1583  $\text{cm}^{-1}$ ), monodentate nitrate (1447  $\text{cm}^{-1}$ ) and adsorbed  $\text{N}_2\text{O}_3$  (1684  $\text{cm}^{-1}$ ). When  $\text{C}_3\text{H}_6$  is added to the feed, new bands at 1676 and 1594  $\text{cm}^{-1}$  have appeared which are assigned to  $\nu(\text{C}=\text{O})$  and  $\nu(\text{C}=\text{C})$  bands of polyene, respectively. A weak band at 1480  $\text{cm}^{-1}$  is also observed, which can be ascribed to  $\nu_{as}(\text{NO}_2)$ . It can be seen that the formation of adsorbed  $\text{NO}_x$  species is sharply depressed when  $\text{C}_3\text{H}_6$  is present, which may be due to occupation of adsorption



**Fig. 7.** IR spectra for Fe-Beta (A), FMC1 (B) and  $\text{MnO}_x/\text{CeO}_2$  (C) after exposure to 500 ppm  $\text{NO}/10\% \text{O}_2/\text{He}$  or 500 ppm  $\text{NO}/10\% \text{O}_2/500 \text{ ppm } \text{C}_3\text{H}_6/\text{He}$  at 150 °C for 30 min.





**Fig. 8.** MS data for Fe-Beta (A) and FMC1 (C) exposed to 500 ppm NO/10% O<sub>2</sub>/Ar at RT followed by heating in a flow of Ar at 10 °C/min, and Fe-Beta (B) and FMC1 (D) exposed to 500 ppm NO/500 ppm C<sub>3</sub>H<sub>6</sub>/10% O<sub>2</sub>/Ar at RT followed by heating in a flow of Ar at 10 °C/min.

**Table 2**

The amount of each species during TPD experiments.

Reaction process	Species	The amount of species (mmol/g <sub>cat</sub> )	
		Fe-Beta	FMC1
NO + O <sub>2</sub> -Adsorption	NO	0.837	0.416
C <sub>3</sub> H <sub>6</sub> -Adsorption	C <sub>3</sub> H <sub>6</sub>	2.242	0.961
NO + O <sub>2</sub> + C <sub>3</sub> H <sub>6</sub> -Adsorption	NO	0.223	0.251
	C <sub>3</sub> H <sub>6</sub>	0.782	0.387
NH <sub>3</sub> -TPD	NH <sub>3</sub>	1.175	0.428

sites by the polymerized C<sub>3</sub>H<sub>6</sub> species. On FMC1, bands at 1280, 1571 and 1629 cm<sup>-1</sup> are observed when NO + O<sub>2</sub> is introduced, as displayed in Fig. 7(B). The band at 1280 cm<sup>-1</sup> is attributed to  $\nu(\text{NO}_3^-)$ , while the bands at 1571 and 1629 cm<sup>-1</sup> are due to monodentate and bridged nitrates. When C<sub>3</sub>H<sub>6</sub> is present, new bands assigned to  $\nu_s(\text{COO})$  (1574 cm<sup>-1</sup>) and  $\nu(\text{C=O})$  (1670 cm<sup>-1</sup>) have emerged, arising from

partial oxidation of C<sub>3</sub>H<sub>6</sub> on the catalyst surface. Meanwhile, bands at 1430 and 1313 cm<sup>-1</sup> have developed, attributed to monodentate nitrates and bidentate nitrites [37–51].

Turning to the MnO<sub>x</sub>/CeO<sub>2</sub> sample, bands at 1530 cm<sup>-1</sup> and 1280 cm<sup>-1</sup> are formed in the absence of C<sub>3</sub>H<sub>6</sub> that can be assigned to  $\nu(\text{NO}_3^-)$  (see in Fig. 7(C)). When C<sub>3</sub>H<sub>6</sub> is added to the feed gas, carboxyl species (1570 cm<sup>-1</sup>) are formed, although the bands belonging to  $\nu(\text{NO}_3^-)$  at 1530 and 1280 cm<sup>-1</sup> are still observed. From the foregoing results, it is clear that C<sub>3</sub>H<sub>6</sub> is partially oxidized over the MnO<sub>x</sub>/CeO<sub>2</sub> sample, whereas it polymerizes on Fe-Beta, blocking the sites for NO<sub>x</sub> adsorption and becoming the dominant species on the surface.

Blocking of the NO<sub>x</sub> adsorption sites on Fe-Beta by C<sub>3</sub>H<sub>6</sub> is also evidenced by NO<sub>x</sub>-TPD (Fig. 8) and the amount of each gaseous species desorbed being listed in Table 2. After saturation by the reactant gases, the samples are heated from room temperature to 700 °C in Ar. For Fe-Beta zeolite, NO ( $m/z = 30$ ) has evolved as two peaks regardless of whether C<sub>3</sub>H<sub>6</sub> is present during the adsorption step. Integration of the peaks shows that the amount of NO<sub>x</sub> desorbed has decreased when C<sub>3</sub>H<sub>6</sub>

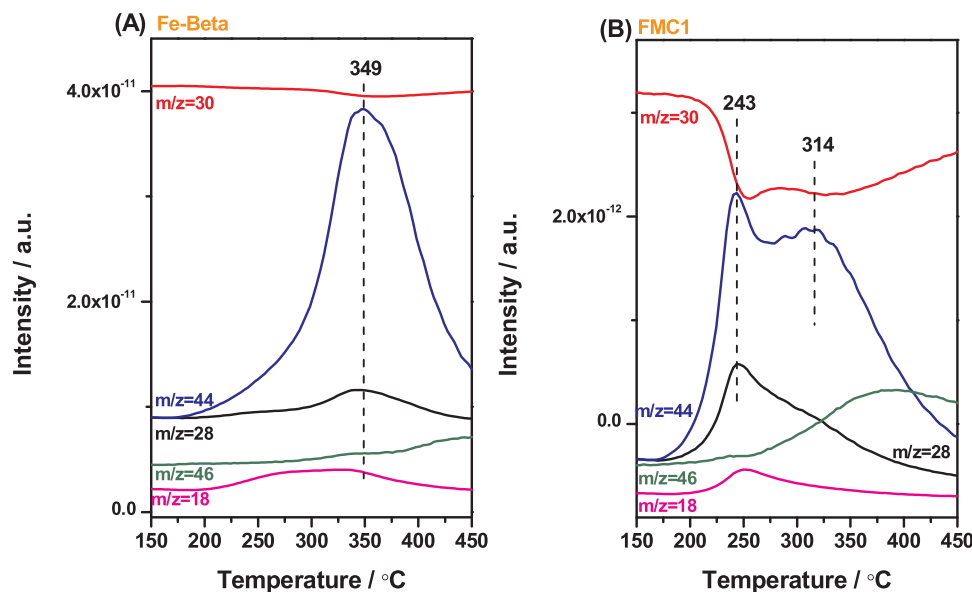


Fig. 9. MS signal obtained over (A) Fe-Beta and (B) FMC1 catalysts in 500 ppm NO/10% O<sub>2</sub>/Ar after C<sub>3</sub>H<sub>6</sub> adsorption using 500 ppm C<sub>3</sub>H<sub>6</sub>/Ar for 30 min; C<sub>3</sub>H<sub>6</sub> adsorption was performed at 150 °C.

is present in the adsorption step, indicating that the adsorption of NO<sub>x</sub> is inhibited by C<sub>3</sub>H<sub>6</sub>. Moreover, the NO<sub>x</sub> desorbs at relatively low temperatures when C<sub>3</sub>H<sub>6</sub> is present, suggesting that C<sub>3</sub>H<sub>6</sub> blocks the strong adsorption sites for NO<sub>x</sub> [52]. Moreover, minimal desorption of C<sub>3</sub>H<sub>6</sub> is observed (Fig. S5), indicating that C<sub>3</sub>H<sub>6</sub> is strongly bonded to the zeolite surface, this being in line with the DRIFTS data indicating that polymerization of C<sub>3</sub>H<sub>6</sub> has occurred on Fe-Beta. For the hybrid catalyst, however, the presence of C<sub>3</sub>H<sub>6</sub> during NO<sub>x</sub> adsorption has less effect on the amount of NO<sub>x</sub> subsequently desorbed during TPD than for Fe-Beta, albeit NO<sub>x</sub> desorption above 300 °C is depressed to some degree. Additionally, gaseous CO<sub>2</sub> is generated at temperatures in excess of 400 °C, consistent with the higher oxidative capability of MnO<sub>x</sub>/CeO<sub>2</sub> component in C<sub>3</sub>H<sub>6</sub> oxidation.

### 3.5. Reaction between nitrogen oxides and propene adspecies

In order to evaluate whether or not the intermediates formed through C<sub>3</sub>H<sub>6</sub> adsorption can be eliminated under SCR conditions, the catalyst samples are exposed to NO + O<sub>2</sub> after an initial saturation with C<sub>3</sub>H<sub>6</sub>, after which the temperature being raised from 150 °C to 450 °C. As indicated previously, C<sub>3</sub>H<sub>6</sub> adsorption can result in the formation of various intermediates, C=O and COO species being present on FMC1, while polyene is mostly formed on the Fe-Beta surface (as shown in Fig. S6). As recorded in Fig. 9, during the temperature ramp, consumption peaks for NO can be clearly observed at 243 °C and 314 °C over FMC1, meanwhile the generation of CO<sub>2</sub> ( $m/z = 44$ ) can be observed along with NO consumption. As to the peak at  $m/z = 28$ , it is reasonable to believe that it should belong to the production of N<sub>2</sub> due to the consumption of NO. From these results it can be concluded that upon increase of the temperature, C<sub>3</sub>H<sub>6</sub>-derived species can react with NO to produce N<sub>2</sub> and CO<sub>2</sub>. In contrast, only trace amounts of NO consumption accompanied by a large CO<sub>2</sub> production peak can be detected over Fe-Beta catalyst at 349 °C, indicating that the polyene species on the Fe-Beta surface are apt to oxidize to CO<sub>2</sub> and H<sub>2</sub>O rather than reacting with NO. The fact that NO consumption and N<sub>2</sub> production occur at lower temperatures over FMC1 than on Fe-Beta is consistent with the superior oxidation activity of the mixed oxide in FMC1, leading to the generation of reactive surface oxygenates.

### 3.6. Reaction between ammonia adspecies and nitrogen oxides

Combined DRIFTS and MS measurements have been employed to study the reaction between ammonia adspecies and nitrogen oxides. The catalysts are first exposed to NH<sub>3</sub>/He at 150 °C for 30 min followed by He purging. Next, NO/O<sub>2</sub>/C<sub>3</sub>H<sub>6</sub>/He is introduced, the results being shown in Fig. 10. Adsorbed NH<sub>3</sub> species have given rise to bands at 1485 cm<sup>-1</sup> assigned to NH<sub>4</sub><sup>+</sup> species, and at 1603 cm<sup>-1</sup>, arising from NH<sub>3</sub> coordinated to the Fe-Beta and FMC1 surfaces. Upon introduction of NO + O<sub>2</sub> + C<sub>3</sub>H<sub>6</sub>, bands at 1594 and 1695 cm<sup>-1</sup> have appeared in the case of Fe-Beta, together with a shoulder at 1668 and a band at 2926 cm<sup>-1</sup>. These bands can be assigned to  $\nu(\text{C}=\text{C})$  in polyene species,  $\nu(\text{C}=\text{O})$ , adsorbed NO<sub>2</sub> and  $\nu(\text{CH}_3)$ , respectively. Notably, the band belonging to NH<sub>3</sub> adsorbed on Brønsted acid sites (1485 cm<sup>-1</sup>) has initially decreased due to the reaction of NH<sub>4</sub><sup>+</sup> with adsorbed NO<sub>x</sub>, as evidenced by the production of N<sub>2</sub> ( $m/z = 28$ ) as shown in Fig. 10. However, the band intensity has reached a fairly constant value quickly, which may be the result of C<sub>3</sub>H<sub>6</sub> inhibition on NO<sub>x</sub> adsorption. In contrast, over the FMC1 catalyst, the introduction of NO + O<sub>2</sub> + C<sub>3</sub>H<sub>6</sub> has caused the disappearance of adsorbed NH<sub>3</sub> species (1474, 1617 cm<sup>-1</sup>), while several new bands at 1678, 1572, 1432 and 1334 cm<sup>-1</sup> have increased in intensity with time. These bands can be assigned to  $\nu(\text{C}=\text{O})$ ,  $\nu_{\text{as}}(\text{COO})$ ,  $\nu_{\text{as}}(\text{COO})$  and bidentate nitrites, respectively. Comparing the gas phase products detected by MS, much larger amount of N<sub>2</sub>, H<sub>2</sub>O and CO<sub>2</sub> are generated over FMC1, this being in line with its superior NH<sub>3</sub>-SCR activity compared to Fe-Beta when C<sub>3</sub>H<sub>6</sub> is present. It is also worth noting that over the FMC1 sample, two events are observed which may give rise to a peak at  $m/z = 28$ . The first event is assigned to the generation of N<sub>2</sub> on the FMC1 surface during switching of the feed gas, while the other is associated with the formation of CO<sub>x</sub> from C<sub>3</sub>H<sub>6</sub> oxidation which gives rise to signals at 44 and 28 (due to CO<sub>2</sub> fragmentation in the MS).

### 3.7. Stability of intermediates

After exposure of the NH<sub>3</sub>-loaded samples to NO + O<sub>2</sub> + C<sub>3</sub>H<sub>6</sub>, the catalysts are heated from 150 °C to the desired temperature in Ar in order to study the stability of the intermediates present. As shown in Fig. 11, it can be inferred that mainly polyene and C=O species have been present on the Fe-Beta surface, the intensity of these bands showing little change as the temperature has raised from 150 °C to

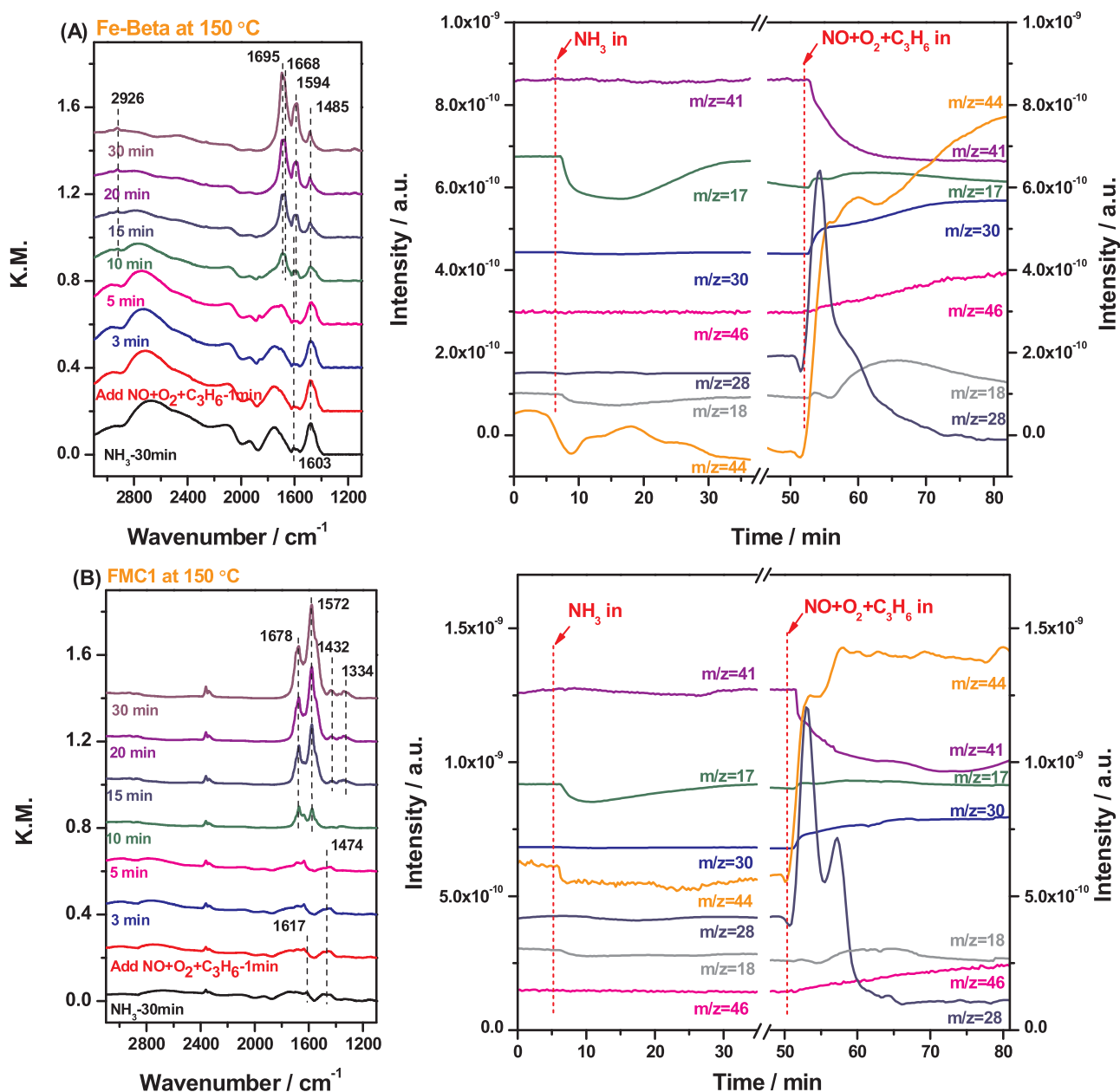


Fig. 10. IR spectra (left panel) and MS data (right panel) for (A) Fe-Beta and (B) FMC1 pretreated by exposure to 500 ppm  $\text{NH}_3/\text{Ar}$  followed by exposure to 500 ppm  $\text{C}_3\text{H}_6/500$  ppm  $\text{NO}/10\%$   $\text{O}_2/\text{Ar}$  at  $150^\circ\text{C}$  for various times.

$200^\circ\text{C}$ . With further increase of the temperature, the band belonging to  $\nu(\text{C}=\text{O})$  decreases in intensity while gaseous  $\text{CO}$  is detected by MS (depicted in Fig. S7). The band belonging to adsorbed  $\text{NO}_2$  at  $1668\text{ cm}^{-1}$  also diminishes and at the same time a band at  $1880\text{ cm}^{-1}$  assigned to gaseous  $\text{NO}$  arises indicative of nitrite decomposition. However, changes in the MS signal at  $m/z = 30$  are hard to detect, presumably due to the low  $\text{NO}$  concentration (shown in Fig. S7). Notably, the bands at  $1594\text{ cm}^{-1}$  and  $2923\text{ cm}^{-1}$  assigned to  $\nu(\text{C}=\text{C})$  in polyene and  $\nu(\text{CH}_3)$ , respectively, are barely changed. From this it can be inferred that upon adsorption on Fe-Beta,  $\text{C}_3\text{H}_6$  transforms to polymerized species, even at low temperature ( $150^\circ\text{C}$ ). Indeed, these species are difficult to eliminate below  $300^\circ\text{C}$ , and can therefore inhibit SCR activity. For FMC1, the  $\nu(\text{C}=\text{O})$  band ( $1678\text{ cm}^{-1}$ ) has decreased in intensity with increase of the temperature, while the  $\nu(\text{COO})$  band ( $1432\text{ cm}^{-1}$ ) has increased in intensity up to  $250^\circ\text{C}$  and then decreased above  $300^\circ\text{C}$ . This phenomenon can be explained on the basis that the  $\text{C}=\text{O}$  species first convert to  $\text{COO}$  species, the latter undergoing further

oxidation to gaseous  $\text{CO}_2$  upon increase of the temperature. This is substantiated by MS data shown in the inset of Fig. 11,  $\text{CO}_2$  being evolved in two main steps at  $250^\circ\text{C}$ – $350^\circ\text{C}$ .

#### 4. Discussion

According to the literature, unburned hydrocarbons (HCs) in diesel engine exhaust of which propene (kinetic diameter of  $4.5\text{ \AA}$ ) is a typical constituent - can deactivate zeolites such as ZSM-5 and BEA (possessing pore diameters of approximately of  $5.5\text{ \AA}$  and  $6.5\text{ \AA}$ , respectively [10,16]). It is generally accepted that the carbonaceous deposits formed from adsorbed HCs can block the active sites of the catalyst [11,17], although little is known about the exact composition of these deposits. Previous results demonstrate that coke formation is mainly related to the pore structure and acidity of the zeolite [17]. Zeolites with larger pore size ( $> 4.5\text{ \AA}$ ) and strong acidity are more susceptible to deactivation by  $\text{C}_3\text{H}_6$ . The degradation of catalyst activity can also be ascribed



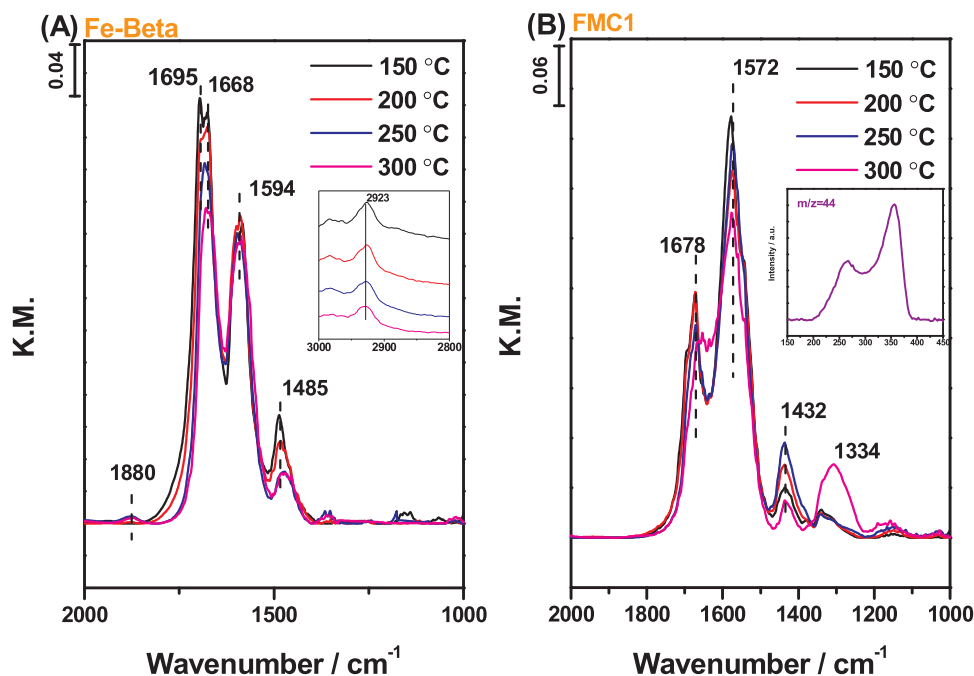


Fig. 11. IR spectra showing consumption of intermediates over (A) Fe-Beta and (B) FMC1 in flowing Ar at different temperatures after exposure to 500 ppm  $\text{NH}_3$ /500 ppm  $\text{NO}$ /10%  $\text{O}_2$ /500 ppm  $\text{C}_3\text{H}_6$ /Ar at 150 °C.

to the competitive adsorption of  $\text{C}_3\text{H}_6$  with  $\text{NH}_3$  and/or  $\text{NO}$  on the catalyst surface, whereby the formation of intermediates during the  $\text{NH}_3$ -SCR reaction is inhibited [10]. In order to alleviate the effect of  $\text{C}_3\text{H}_6$ , Ma et al. [10] have designed a Fe-BEA monolith catalyst coating modified with MOR to restrict the diffusion of  $\text{C}_3\text{H}_6$  in BEA cavities and reduce the surface acidity, thereby improving the tolerance of the catalyst towards HCs. Zhang et al. [3] have synthesized a core-shell structured meso-SSZ-13 material by combining controlled desilication with subsequent self-assembly, resulting in a material with smaller pores than the kinetic diameter of propene, thereby inhibiting direct access of propene to the zeolite channels. These workers have also found that due to the coverage of the external surface by the shell, the amount of exposed sites for propene oxidation is decreased, effectively reducing propene polymerization. The use of additives is another effective method to improve the hydrocarbon resistance of HBEA-based catalysts. Feng et al. [14] have used incipient wetness impregnation to prepare CuFe/Ce/Beta. By adding Ce, the presence of strong acid sites is suppressed, which acting as the main adsorption sites for propene. Shi et al. [17] have used  $\text{CeO}_2$  as an additive to minimize the poisoning effects of propene on HBEA. The external surface of HBEA is coated by  $\text{CeO}_2$  forming a core-shell structure, and it is shown that the improved resistance to propene poisoning is due to a combination of (i) decreased  $\text{C}_3\text{H}_6$  adsorption and (ii)  $\text{C}_3\text{H}_6$  oxidation by the ceria. Overall, while some progress has been made towards improving the hydrocarbon resistance of zeolite catalysts, the exact nature of the species acting as poisons is unclear, while considerable scope exists to improve catalyst activity further.

In the present work, we have designed and synthesized hybrid catalysts exemplified by FMC1. During calcination, a chemical interaction arose between the mechanically mixed Fe-Beta and  $\text{MnO}_x/\text{CeO}_2$ . Specifically, a new phase corresponding to  $(\text{Mn}_{0.983}\text{Fe}_{0.017})_2\text{O}_3$  was formed, while the redox properties of the hybrid catalyst were modified as evidenced by  $\text{H}_2$ -TPR (Fig. 2). FMC1 catalyst, being enriched with  $\text{Mn}^{3+}$ , exhibits relatively fewer active oxygen species that are reduced at low temperature (302 °C in  $\text{H}_2$ -TPR). Comparatively, the  $\text{MnO}_x/\text{CeO}_2$  sample, which is characterized by a higher concentration of  $\text{Mn}^{4+}$  and active oxygen species, has better catalytic activity in both  $\text{C}_3\text{H}_6$  oxidation (Fig. 5(B)) and  $\text{NH}_3$  oxidation, although the latter reaction leads

to relatively lower high temperature  $\text{NO}_x$  conversion and increased  $\text{N}_2\text{O}$  generation. The hybrid FMC catalysts exhibit excellent SCR activity across the whole temperature window and the ratio of the zeolite to oxide can be tuned according to the requirements of the application (as shown in Fig. 1): higher fractions of the oxide component provide better low temperature activity but higher  $\text{N}_2\text{O}$  yield and lower  $\text{NO}_x$  conversion at high temperature. The results imply that the higher oxidation activity associated with higher fractions of the oxide component leads to better low temperature  $\text{NH}_3$ -SCR activity, indicating that  $\text{NO}$  oxidation to  $\text{NO}_2$  represents the rate limiting step for the low-temperature SCR reaction. Higher amounts of  $\text{Mn}^{4+}$  favor  $\text{NO}$  oxidation, and therefore facilitate the low-temperature SCR reaction.

In order to ascertain the function of  $\text{MnO}_x/\text{CeO}_2$  in the hybrid catalyst, mechanistic studies have been conducted. We have observed that the improvement in activity achieved by catalyst FMC1 is not due to direct participation in  $\text{C}_3\text{H}_6$ -SCR or  $\text{C}_3\text{H}_6$  combustion by  $\text{MnO}_x/\text{CeO}_2$ .

As  $\text{C}_3\text{H}_6$  is present in the feed gas,  $\text{C}_3\text{H}_6$  polymerization has readily occurred on the Fe-Beta surface due to its abundant acid sites, blocking the sites for  $\text{NO}$  adsorption and further reaction. After combining the oxidation components with Fe-Beta, the partial oxidation of  $\text{C}_3\text{H}_6$  to oxygenates occurs more readily than polymerization as shown in Fig. 6, and thus the catalyst surface is not subject to fouling. Besides that, due to the higher oxidation activity of  $\text{MnO}_x/\text{CeO}_2$  compared to Fe-Beta, the hybrid catalyst can generate more intermediates containing  $\text{C}=\text{O}$  and  $\text{COO}$  functionalities during  $\text{C}_3\text{H}_6$  adsorption than on Fe-Beta, and these oxygenate species are able to react with  $\text{NO}_x$  on FMC1 to enhance the overall activity. Such improvement in activity is further evidenced by the results of combined DRIFTS and MS experiments shown in Fig. 10. However, polyene species generated on Fe-Beta surface hardly react with  $\text{NO}$ , but are directly oxidized to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  at elevated temperatures (349 °C, Fig. 9). Since the surface polymer species are difficult to eliminate at temperatures below 300 °C (shown in Fig. 11), the SCR activity is severely inhibited. Based on the foregoing, it is clear that mixing Fe-Beta zeolite with  $\text{MnO}_x/\text{CeO}_2$  oxide enhanced the oxidation ability of the catalysts. Thus, the much higher oxidative capability of FMC1 can not only partially oxidize  $\text{C}_3\text{H}_6$  into oxygenates, but also enables the reaction of  $\text{C}_3\text{H}_6$ -derived species with  $\text{NO}$  at low temperatures, thereby mitigating the effects of  $\text{C}_3\text{H}_6$  on the  $\text{NH}_3$ -SCR of  $\text{NO}_x$ .

over Fe-Beta catalysts.

## 5. Conclusions

The presence of  $C_3H_6$  during  $NH_3$ -SCR is known to depress the activity of zeolite catalysts with medium to large pores such as metal ion exchanged Beta and ZSM-5 due to fouling and pore blocking. Herein, we propose a simple and effective protocol to mitigate this poisoning effect by mechanically mixing the zeolite with an oxidation catalyst. The resulting FMC1 sample exhibits excellent SCR activity in the presence of  $C_3H_6$  across the whole temperature window.  $MnO_x/CeO_2$  in the hybrid catalysts plays several important roles: 1) converting  $C_3H_6$  into oxygenated intermediates, thereby avoiding polymerization reactions on the zeolite surface and associated pore blocking; 2) reducing the competitive adsorption between  $NO_x$  and  $C_3H_6$  to facilitate the  $NH_3$ -SCR reaction; 3) catalyzing the reaction of oxygenates and  $NO_x$  at low temperatures to improve the overall  $NO_x$  conversion activity.

## Acknowledgement

Thanks Doctor U. Mueller from BASF for providing the BEA zeolite support. The work was supported by the National Key R&D Program of China (No. 2017YFA0700103), and National Natural Science Foundation of China (Nos. 21577013 and 21707015).

## Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcatb.2018.09.072>.

## References

- [1] Y. Zhu, B. Chen, R. Zhao, Q. Zhao, H. Gies, F. Xiao, D. Vos, T. Yokoi, X. Bao, U. Kolb, M. Feyen, S. Maurer, A. Moini, U. Müller, C. Shi, W. Zhang, *Catal. Sci. Technol.* 6 (2016) 6581–6592.
- [2] S. Brandenberger, O. Kröcher, A. Tissler, R. Althoff, *Appl. Catal. B* 95 (2010) 348–357.
- [3] T. Zhang, F. Qiu, J. Li, *Appl. Catal. B* 195 (2016) 48–58.
- [4] R. Nedyalkova, S. Shwan, M. Skoglundh, L. Olsson, *Appl. Catal. B* 138–139 (2013) 373–380.
- [5] L. Xu, C. Shi, B. Chen, Q. Zhao, Y. Zhu, H. Gies, F. Xiao, D. De Vos, T. Yokoi, X. Bao, U. Kolb, M. Feyen, S. Maurer, A. Moini, U. Müller, W. Zhang, *Microporous Mesoporous Mater.* 236 (2016) 211–217.
- [6] P. Balle, B. Geiger, D. Klukowski, M. Pignatelli, S. Wohnrau, M. Menzel, I. Zirkwa, G. Brunklaus, S. Kureti, *Appl. Catal. B* 91 (2009) 587–595.
- [7] L. Xu, C. Shi, Z. Zhang, H. Gies, F. Xiao, D. Vos, T. Yokoi, X. Bao, M. Feyen, S. Maurer, B. Yilmaz, U. Müller, W. Zhang, *Microporous Mesoporous Mater.* 200 (2014) 304–310.
- [8] P. Sazama, B. Wichterlová, Š. Sklenák, V. Parvulescu, N. Candu, G. Sádovská, J. Dědeček, P. Klein, V. Pashkova, P. Štastný, *J. Catal.* 318 (2014) 22–33.
- [9] R. Zhang, N. Liu, Z. Lei, B. Chen, *Chem. Rev.* 116 (2016) 3658–3721.
- [10] L. Ma, J. Li, Y. Cheng, C. Lambert, L. Fu, *Environ. Sci. Technol.* 46 (2012) 1747–1754.
- [11] L. Ma, W. Su, Z. Li, J. Li, L. Fu, J. Hao, *Catal. Today* 245 (2015) 16–21.
- [12] C. He, Y. Wang, Y. Cheng, C. Lambert, R. Yang, *Appl. Catal. A Gen.* 368 (2009) 121–126.
- [13] I. Malpartida, O. Marie, P. Bazin, M. Daturi, X. Jeandel, *Appl. Catal. B* 102 (2011) 190–200.
- [14] X. Feng, Y. Cao, L. Lan, C. Lin, Y. Li, H. Xu, M. Gong, Y. Chen, *Chem. Eng. J.* 302 (2016) 697–706.
- [15] I. Heo, Y. Lee, I. Nam, J. Choung, J. Lee, H. Kim, *Microporous Mesoporous Mater.* 141 (2011) 8–15.
- [16] J. Li, R. Zhu, Y. Cheng, C. Lambert, R. Yang, *Environ. Sci. Technol.* 44 (2010) 1799–1805.
- [17] Y. Shi, X. Wang, Y. Xia, C. Sun, C. Zhao, S. Li, W. Li, *Mol. Catal.* 433 (2017) 265–273.
- [18] J. Luo, A. Yezerets, C. Henry, H. Hess, K. Kamasamudram, H. Chen, W. Epling, *Hydrocarbon Poisoning of Cu-Zeolite SCR Catalysts*, SAE International, 2012.
- [19] C. Liu, J. Shi, C. Gao, C. Niu, *Appl. Catal. A Gen.* 522 (2016) 54–69.
- [20] D. Delimaris, T. Ioannides, *Appl. Catal. B* 84 (2008) 303–312.
- [21] X. Tang, Y. Li, X. Huang, Y. Xu, H. Zhu, J. Wang, W. Shen, *Appl. Catal. B* 62 (2006) 265–273.
- [22] S. Jiang, R. Zhou, *Fuel Process. Technol.* 133 (2015) 220–226.
- [23] R. Jin, Y. Liu, Y. Wang, W. Cen, Z. Wu, H. Wang, X. Weng, *Appl. Catal. B* 148–149 (2014) 582–588.
- [24] L. France, Q. Yang, W. Li, Z. Chen, J. Guang, D. Guo, L. Wang, X. Li, *Appl. Catal. B* 206 (2017) 203–215.
- [25] B. Xie, J. Song, L. Ren, Y. Ji, J. Li, F. Xiao, *Chem. Mater.* 20 (2008) 4533–4535.
- [26] B. Chen, C. Shi, M. Crocker, Y. Wang, A. Zhu, *Appl. Catal. B* 132–133 (2013) 245–255.
- [27] M. Salazar, R. Becker, W. Grünert, *Appl. Catal. B* 165 (2015) 316–327.
- [28] H. Chen, A. Sayari, A. Adnot, F. Larachi, *Appl. Catal. B* 32 (2001) 195–204.
- [29] S. Deng, H. Liu, W. Zhou, J. Huang, G. Yu, J. Hazard. Mater. 186 (2011) 1360–1366.
- [30] T. Rao, M. Shen, L. Jia, J. Hao, J. Wang, *Catal. Commun.* 8 (2007) 1743–1747.
- [31] Z. Liu, Y. Yi, S. Zhang, T. Zhu, J. Zhu, J. Wang, *Catal. Today* 216 (2013) 76–81.
- [32] B. Tan, K. Klabunde, P. Sherwood, *J. Am. Chem. Soc.* 113 (1991) 855–861.
- [33] G. Qi, R. Yang, *J. Phys. Chem. B* 108 (2004) 15738–15747.
- [34] Z. Zhang, B. Chen, X. Wang, L. Xu, C. Au, C. Shi, M. Crocker, *Appl. Catal. B* 165 (2015) 232–244.
- [35] G. Qi, R. Yang, R. Chang, *Appl. Catal. B* 51 (2004) 93–106.
- [36] Z. Wu, R. Jin, H. Wang, Y. Liu, *Catal. Commun.* 10 (2009) 935–939.
- [37] P. Kumar, M. Reddy, B. Hyun-Sook, H. Phil, *Catal. Letters* 131 (2009) 85–97.
- [38] F. Dorado, P. García, A. Lucas, M. Ramos, A. Romero, *J. Mol. Catal. A Chem.* 332 (2010) 45–52.
- [39] V. Matyshak, O. Krylov, *Catal. Today* 25 (1995) 1–87.
- [40] R. Long, R. Yang, *J. Phys. Chem. B* 103 (1999) 2232–2238.
- [41] N. Hayes, R. Joyner, E. Shpiro, *Appl. Catal. B* 8 (1996) 343–363.
- [42] S. Park, Y. Park, S. Park, L. Kevan, *J. Chem. Soc. Faraday Trans. 2* (2000) 5500–5509.
- [43] I. Cayirtepe, A. Naydenov, G. Ivanov, M. Kantcheva, *Catal. Letters* 132 (2009) 438–449.
- [44] L. Li, N. Guan, *Microporous Mesoporous Mater.* 117 (2009) 450–457.
- [45] J. Liu, X. Li, Q. Zhao, C. Hao, D. Zhang, *Environ. Sci. Technol.* 47 (2013) 4528–4535.
- [46] K. Góra-Marek, K. Brylewska, K. Tarach, M. Rutkowska, M. Jabłońska, M. Choi, L. Chmielarz, *Appl. Catal. B* 179 (2015) 589–598.
- [47] R. Long, R. Yang, *J. Catal.* 207 (2002) 274–285.
- [48] G. Qi, *J. Catal.* 226 (2004) 120–128.
- [49] L. Xu, X. Li, M. Crocker, Z. Zhang, A. Zhu, C. Shi, *J. Mol. Catal. A Chem.* 378 (2013) 82–90.
- [50] F. Prinetto, G. Ghiotti, I. Nova, L. Lietti, E. Tronconi, P. Forzatti, *J. Phys. Chem. B* 105 (2001) 12732–12745.
- [51] Z. Zhang, L. Chen, Z. Li, P. Li, F. Yuan, X. Niu, Y. Zhu, *Catal. Sci. Technol.* 6 (2016) 7151–7162.
- [52] M. Iwasaki, K. Yamazaki, K. Banno, H. Shinjoh, *J. Catal.* 260 (2008) 205–216.